



# Effect of additives on electrochemical performance of lithium nickel cobalt manganese oxide at high temperature



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## HIGHLIGHTS

- Several types of additives were attempted to enhance the structural stability of high-Ni-content ( $\text{Ni} \geq 60\%$ ) cathodes.
- Interpretation of cycle performance in connection with SEM, *in situ* monitoring of cell pressure, FT-IR, OCV changes.
- 1,3-Propane sulfone is highly desirable for enhancing the electrochemical performance of Ni-rich cathodes.

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## ABSTRACT

Lithium–nickel–cobalt–manganese oxide,  $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$  (NCM) is a low-cost cathode material with a high capacity and a moderately high rate capability, however, it still suffers from poor electrochemical performance. In this study, several types of additives are attempted to enhance the surface stability of high-Ni-content ( $\text{Ni} \geq 60\%$ ) cathodes and the most effective additive turns out to be PS. The cycle performance in the presence of 2% PS is much improved at a high temperature of 60 °C: (1) 98.9% of its initial capacity is preserved, (2) the increase in thickness is only 17.9%, preventing undesired swellings, and (3) gases are not generated in large amounts with the internal pressure being 56.4 kPa. The FT-IR spectroscopy results suggest that the surface of the cathode in the presence of 2% PS is covered with a film of alkyl sulfone components (RSOSR and  $\text{RSO}_2\text{SR}$ ), which is possibly formed by the electrochemical oxidation of PS. The current results confirm that the electrochemical performance of Ni-rich cathodes can be improved via the appropriate use of additives. They also indicate that among the tested additive candidates in this study, PS is highly desirable for enhancing the electrochemical performance of Ni-rich cathodes.

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## 1. Introduction

Lithium-ion batteries (LIBs), which have undergone rapid commercialization, are considered the most promising energy storage systems owing to their long-term cycle performance and moderate rate capability [1–4]. As demand increases for energy storage systems for large-scale devices such as hybrid electric vehicles (HEVs) and electric vehicles (EVs), further improvement of

the gravimetric and volumetric energy density is recognized as one approach to successfully expand LIB applications [5,6]. In this regard, investigations on various alternative cathodes with high specific capacities are indispensable to achieving high-performance LIBs [7–10]; one attractive cathode material is lithium–nickel–cobalt–manganese oxide,  $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$  (NCM), based on its improved structural stability and low cost [11–15]. The first NCM material developed and commercialized is  $\text{Li}[\text{Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}]\text{O}_2$  (NCM333). It is used to replace  $\text{LiCoO}_2$ , where expensive Co is substituted with cheap Ni and Mn, because of its higher specific capacity and economic advantages [12–15]. The specific capacity of NCM333 (155 mAh  $\text{g}^{-1}$ ), however, is not sufficient to drastically increase the energy density of LIBs, and other alternatives need to be explored. In this regard, NCM materials with high Ni content,

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such as  $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$  (NCM523) and  $\text{Li}[\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}]\text{O}_2$  (NCM622), have been intensively investigated based on their high specific capacities [16–18], however, they always exhibit inferior surface stability, which is particularly the case at elevated temperatures. The deterioration of such cathodes is attributable to the dissolution of metal ions during the electrochemical process because unstable metal ions dissolve easily into the electrolyte. This irreversible reaction leads to a drastic decrease in capacity at high temperatures [19,20]. In addition, the continuous degradation of the cathode generates large amounts of gas owing to the decomposition of the electrolyte and the cathode. As a result, the cell swells considerably, and this type of swelling significantly decreases the safety of LIBs [21,22]. Therefore, improvements in both the surface stability and electrochemical performance of NCM cathodes are essential for ensuring their widespread adoption in LIBs.

In this study, functional additives are investigated to enhance the electrochemical performance by increasing the surface stability of an NCM material containing 60% Ni (NCM622). Previous papers have reported the effects of additives on full cells containing NCM-based cathodes, but these studies have only suggested that the additives are effective for improving the electrochemical performance of the anode through the formation of a desirable solid–electrolyte interface (SEI) on the anode surface [23,24]. None of studies, however, investigated the effects of additives on NCM-based cathodes with high Ni contents at high temperatures, even though these specific effects are important for achieving superior electrochemical performance of LIBs. Therefore, finding a suitable additive as well as identifying its effect on cathode performance and working mechanism are still necessary in order to achieve better electrochemical performance of LIBs.

The following additive candidates with different chemical functionalities were selected: vinylene carbonate (VC, with an alkenyl group), succinonitrile (SN, with a nitrile group), propene sulfone (PST, with sulfone and alkenyl groups), and propane sulfone (PS, with a sulfone group) (The structures of these candidates are shown in Fig. 1a). The underlying concept explored in this study is centered on the modification of the surface properties of NCM-based cathodes: once the additive forms a passivation film on the surface of the NCM-based cathode, it is expected that further decomposition of the electrolyte and cathode at high temperatures will be suppressed as a result of inhibition of undesired contact between them, resulting in enhanced surface stability of the NCM cathode. On the basis of these suppositions, the electrochemical

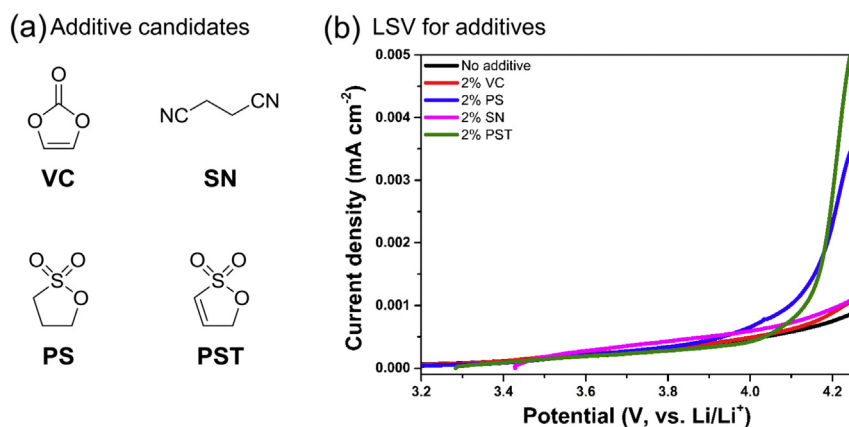
performances of full cells with different additives were evaluated and their failure modes were observed to provide new information on the use of additives to achieve high-performance LIBs.

## 2. Experimental

The electrolytes and additives were provided by PanaxEtec and were used as received without further purification. Linear sweep voltammetry (LSV)-based measurements were performed with an electrochemical workstation (SP-300, Biologic) at a scan rate of  $0.2 \text{ mV s}^{-1}$  using a glassy carbon electrode ( $7.07 \times 10^{-2} \text{ cm}^2$ ) as the working electrode. Lithium foil was used for the counter and reference electrodes. The sweep voltage ranged from 3 to 5 V (vs.  $\text{Li}/\text{Li}^+$ ).

To prepare the anodes, a mixture of the graphite (7  $\mu\text{m}$ , provided by Poscochemtech, Korea), Super P<sup>®</sup> carbon black, carboxymethyl cellulose (CMC) (Cellogen, DKS), and styrene-butadiene rubber (SBR) (BM 400B, Zeon) (in a weight ratio of 96:1:1:2) was dispersed in distilled water. The slurry formed from dispersion was coated on a piece of copper foil, and the resulting electrode plate was dried in a vacuum oven at  $120^\circ\text{C}$  for 12 h. The loading and electrode densities were fixed at  $8.45 \text{ mg cm}^{-2}$  and  $1.50 \text{ g cm}^{-3}$ , respectively. To prepare the cathode, a mixture of  $\text{Li}[\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}]\text{O}_2$  (provided by Ecopro, Korea), polyvinylidene fluoride (PVdF) (KF1100, Kureha), and Super P<sup>®</sup> carbon black (in a weight ratio of 92:4:4) was dispersed in *N*-methyl-2-pyrrolidone (NMP). The formed slurry was coated on a piece of aluminum foil, and the resulting electrode plate was dried in a vacuum oven at  $120^\circ\text{C}$  for 12 h. The loading and electrode densities were fixed at  $14.45 \text{ mg cm}^{-2}$  and  $2.95 \text{ g cm}^{-3}$ , respectively. Galvanostatic discharge–charge cycling was performed using a pouch-type cell (34 mm  $\times$  50 mm in size), which was assembled using the anode, cathode, separator, and electrolyte (mixture of EC/EMC = 3:7 (volume) and 1.15 M  $\text{LiPF}_6$ ). The N/P ratio of the cell was 1.15. Cells containing the various additives (VC, SN, PS, and PST) were fabricated and galvanostatically charged to 4.2 V vs.  $\text{Li}/\text{Li}^+$  and discharged to 3.0 V vs.  $\text{Li}/\text{Li}^+$  repeatedly at a constant current of 0.5 C at  $60^\circ\text{C}$  using a charge/discharge unit (TOSCAT-3100, Toyo).

After the cells were electrochemically characterized, their thicknesses were measured using a thickness gauge (ID-C125XB, Mitutoyo). To analyze the gas generated during the operation of the cells, gas samples from the cells were collected with a 10- $\mu\text{m}$  syringe and analyzed by gas chromatography–mass spectrometry (GC–MS; 7890A, Agilent) in an Ar-filled glove box with  $<0.5 \text{ ppm}$  of  $\text{H}_2\text{O}$  and  $<1 \text{ ppm}$  of  $\text{O}_2$ . The cells were then dismantled, and the electrodes and separators were washed with freshly prepared



**Fig. 1.** (a) Molecular structure of additives tested in this study, (b) Linear sweep voltammetry (LSV) results for additives (Working electrode: glassy carbon, Counter electrode: Li-metal, Reference electrode: Li-metal, Scan rate:  $0.2 \text{ mV s}^{-1}$ ).

dimethyl carbonate (DMC). The surface morphologies of the cathodes were analyzed using field-emission scanning electron microscopy (FESEM; Quanta 3D FEG, FEI). The half-cell performances of the individual cycled  $\text{Li}[\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}]\text{O}_2$  cathodes were evaluated in fresh electrolyte samples using lithium metal foil as the counter and reference electrodes. The measurements were made using a constant current of 1 C at 60 °C (WBC3000, WonATech). For quantification of metal dissolution, three electrode-beaker-type half cells were assembled with different additives and then fully charged to 4.3 V. The cells were kept in a 60 °C oven for 7 days and then they were fully discharged to 3.0 V. Finally, the supernatants were analyzed by inductively coupled plasma mass spectrometry (ICP-MS; aurora 60, Bruker) to quantify dissolution of Ni, Co, and Mn. The surfaces of the cathodes were characterized using an FT-IR spectrometer (VERTEX 70, Bruker) in the attenuated total reflection (ATR) mode under a  $\text{N}_2$  atmosphere in a dry room, where the dew point was below –60 °C. All analytical and electrochemical experiments were performed at room temperature.

Cells for *in situ* gas monitoring were constructed from the charged cathodes (obtained by dismantling the cells in an Ar-filled glove box; state of charge (SOC): 100%) and fresh electrolyte (10  $\mu\text{L}$ ). These cells were heated in a 100 °C oven for 15 h, and the pressure within them was recorded using a pressure sensor (GE).

### 3. Results and discussion

The electrochemical stabilities of the various electrolyte samples measured by LSV are shown in Fig. 1b. Their electrochemical oxidative behavior varied depending on the additives: the electrolyte samples with sulfone-based additives exhibited a high oxidation current at approximately 4.1 V, whereas the samples with VC and SN exhibited relatively lower oxidation currents. All these oxidation currents, however, were slightly higher than that obtained with the additive-free electrolyte. These results confirmed that the additives assisted the formation of a new surface through an electrochemical oxidation reaction.

Prior to the measurement of the cycle performance, the internal behavior of the cell was simulated using a homemade *in situ* pressure-monitoring cell (see Experimental section) under harsh conditions (95 °C with 100% SOC) to determine whether the surface films derived from the additives were effective for stabilization of the cathode at high temperatures (Fig. 2). With increasing storage time at high temperature, the inner pressure of the *in situ* pressure-monitoring cell increased dramatically for 3 h and then increased

slowly up to a total monitoring period of 15 h. The shapes of the pressure curves were identical regardless of the additive used, although the final internal pressures were quite different and depended on the choice of additive. The pressure within the additive-free cell and those in the cells containing VC and SN were relatively high, reaching approximately 65 kPa. In contrast, the sulfone-type additives produced relatively lower internal pressure: the PST cell exhibited a moderate internal pressure of 58.5 kPa, and the lowest internal pressure of 56.4 kPa was observed in the cell cycled with PS. According to the simulation results, it is expected that the sulfone-type additives would be effective for the suppression of gas generation, which is considered evidence of deterioration of NCM-cathodes, resulting in poor cycle performance.

The electrochemical performance of NCM622 at an elevated temperature is in good agreement with the results of the above *in situ* pressure-monitoring tests. The initial voltage profiles in Fig. 3a are identical regardless of additive, however, its cycle life is quite different depending on the additive in the cell (Fig. 3b). The graphite/NCM622 full cell without an additive exhibited significant capacity fading at high temperatures: it retained only 78.2% of its initial discharge capacity after 50 cycles. The cell with VC as the additive also exhibited a considerable loss in discharge capacity, retaining only 90.4% of its initial discharge capacity after 50 cycles. The cells with SN, PS, and PST additives exhibited better capacity

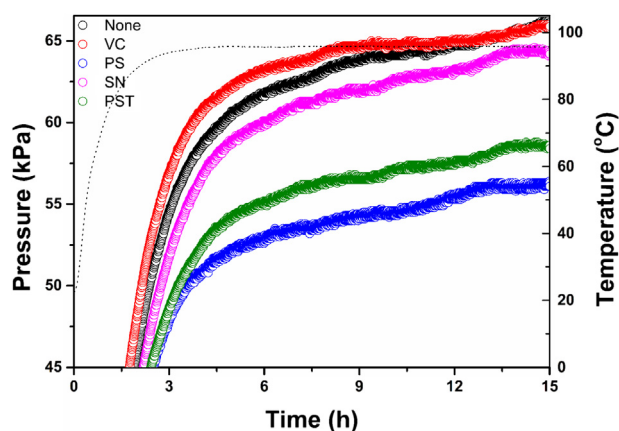
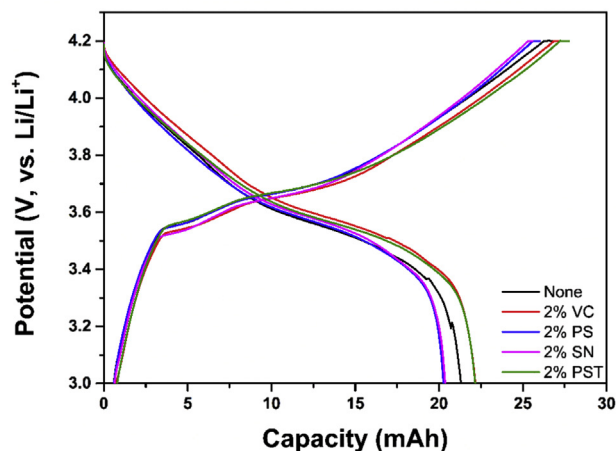


Fig. 2. The results for internal pressure of *in situ* monitoring cell with 100% SOC of NCM622 (The left axis is value of pressure depending on additives and the right axis is temperature for *in situ* pressure-monitoring cell).

(a) Voltage profiles at 1<sup>st</sup> cycle



(b) Retention

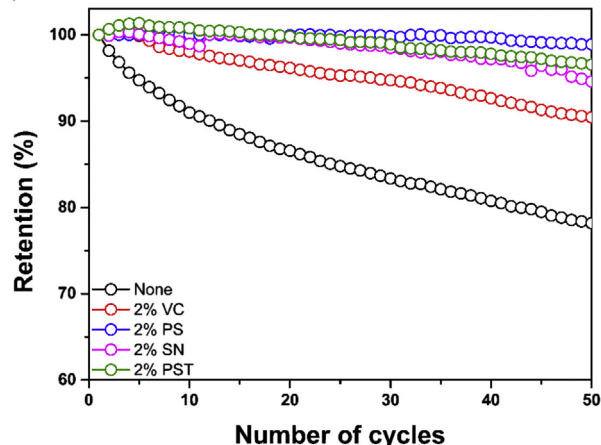


Fig. 3. (a) Voltage profiles for additives at 60 °C (galvanostatic discharge–charge cycling was performed at 3.0–4.2 (V), current density: 0.5 C) (b) Discharge retention of the full-cell depending on additives at 60 °C.

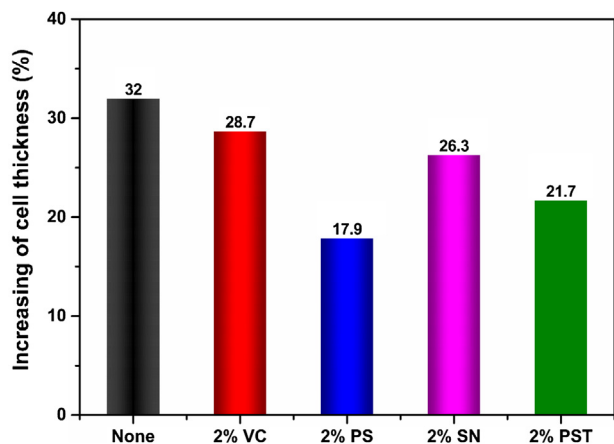


Fig. 4. (a) Thickness changes of pouch full-cell after electrochemical performance at 60 °C.

retention, retaining 94.6%, 98.9%, and 96.6% of their initial capacities, respectively. To differentiate effect of additive on cycle performance of each electrode, additives were evaluated for graphite half-cell (not shown in this manuscript). It was found that they showed comparable specific capacity and retentions which is well agreement with previous literature – capacity fading in full-cell consisting of graphite anode and Ni-rich cathode might be mainly comes from changes in cathode owing to encouraging surface instability [25]. According to results, it can be regarded that difference in cycle performance is attributed to changes in degradation of cathode.

After evaluation of full-cell was completed, the swelling behavior of the cells was measured by thickness gauge in order to correlate with their cycle performance (Fig. 4). The full cell without an additive and that containing VC showed significant increases in thickness (32.0% and 28.7%, respectively) after the electrochemical tests were completed. In contrast, the sulfone-type additives were highly effective in suppressing gas generation: the full cell containing PST underwent an expansion of 21.7%, while the cell containing PS expanded by only 17.9% after cycling. To elucidate the

origin of swelling during the electrochemical cycling, gases in the cell were collected and analyzed by GC–MS (not shown in this manuscript). The results of the analysis indicated the presence of decomposed products from the electrolyte and oxygen, which might have been derived from surface instability of the cathode [21,22]. Based on these results, it is concluded that the electrochemical performance of NCM622 at high temperatures was highly influenced by the internal pressure experienced by the cell during the electrochemical process and that the performance can be improved by utilizing suitable additives.

The fresh and cycled cathodes and separators from the additive-free and PS-containing full cells were observed with FE-SEM, as shown by the images in Fig. 5. It can be seen that the cathode surface of the additive-free cell was completely covered with non-uniform layers that apparently formed because of decomposition owing to electrolyte oxidation. As for the separator, it can be seen that its pores were almost completely blocked owing to electrolyte decomposition. On the other hand, the cathode and separator from the PS-containing cell exhibited different morphologies. Particles of NCM as well as a thin SEI layer can be clearly seen in Fig. 5. In addition, the morphology of the cycled separator was almost identical to that of the fresh separator. This means that PS can be used to control the surface properties of NCM-based cathodes, inhibit electrolyte decomposition, and improve the surface stability, which will directly influence the interfacial characteristics of the cell.

To directly examine the effect of the additives on the cycle performance of the cathodes in the respective cells, the cycled full cells were dismantled and the electrochemical performance of the cathodes was re-evaluated using fresh separators and electrolytes (Fig. 6). All cathodes exhibited loss in capacity compared to their corresponding first-cycle capacities, but their electrochemical characteristics were quite different and depended on the additive used. The most outstanding results were obtained for the cathodes in the PS- and PST-containing cells, with excellent capacity retention values of 94.5% and 93.3%, respectively. This is in contrast to the cathodes in the additive-free (72.5%), VC-containing (82.4%), and SN-containing (85.3%) cells. In addition, the cathodes in the PS- and PST-containing cells exhibited lower degrees of polarization in their voltage profiles. These results indicate that additives have a direct

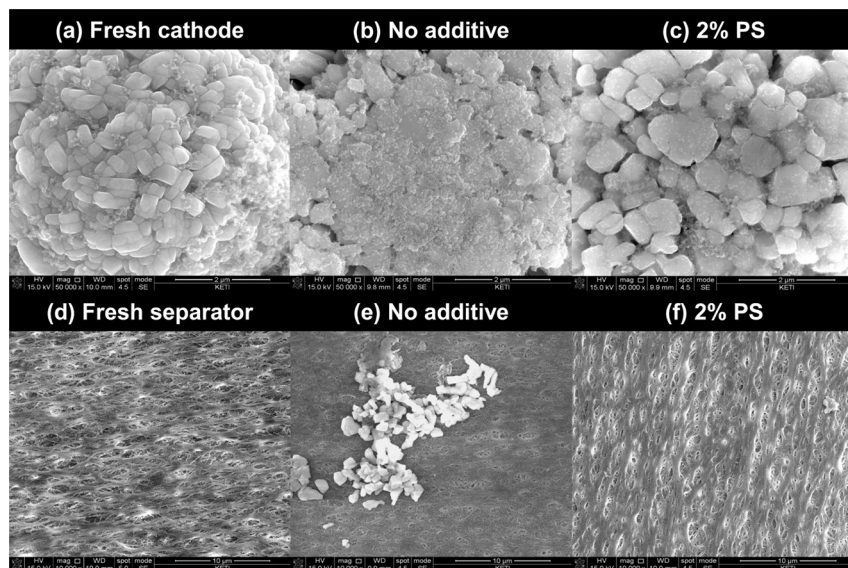
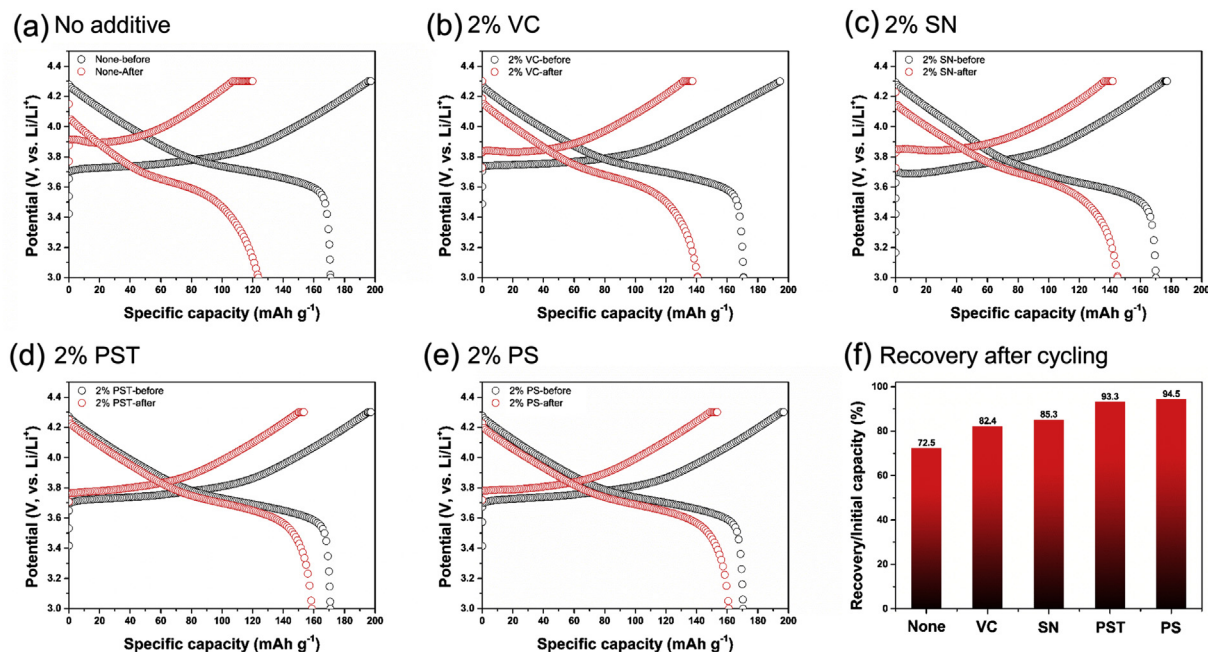


Fig. 5. SEM analysis before and after cycling (a) fresh cathode (b) cathode cycled with no additive (c) cathode cycled with 2% PS (d) fresh separator (e) separator cycled with no additive (f) separator cycled with 2% PS.



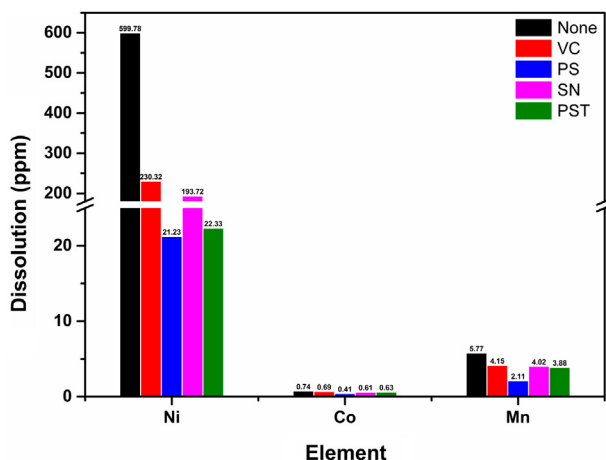


**Fig. 6.** Re-evaluation of cathode after cycling (a) No additive (b) 2% VC (c) 2% SN (d) 2% PST (e) 2% PS (galvanostatic discharge–charge cycling was performed at 3.0–4.3 (V), current density: 0.1 C) (f) Recovery ratio compared to its corresponding first cycle.

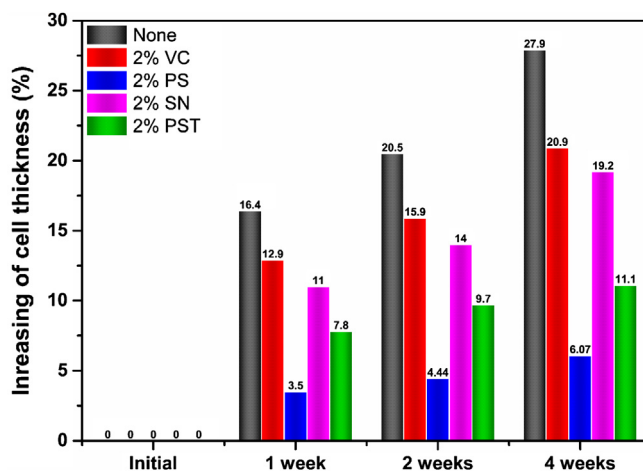
and significant effect on the degree of capacity fading during the electrochemical process and that sulfone-based additives are highly suitable for NCM-based cathodes, as they improve their surface properties, preventing degradation of the cathode. The results for quantification of metal dissolution also provide useful information on changes in the cathode (Fig. 7): dissolution of Ni was relatively higher than that of other metal species including Co and Mn. In addition, it seemed that the dissolution behavior was highly correlated with the additive in the electrolyte: the most efficient ones were PS-type additives (dissolution of Ni was only 21.23 ppm for PS and 22.33 ppm for PST) whereas the cell without additive exhibited considerable amounts of dissolved Ni (599.78 ppm) after the storage test. In effect, many reports indicate that metal dissolution in conjunction with a loss of oxygen in the cathode is one of primary reasons for deterioration of the electrochemical

performance of a Ni-rich system [26–28]. In this respect, utilization of an additive can be considered an effective way to increase the surface stability of the Ni-rich cathode, resulting in its improved electrochemical performance.

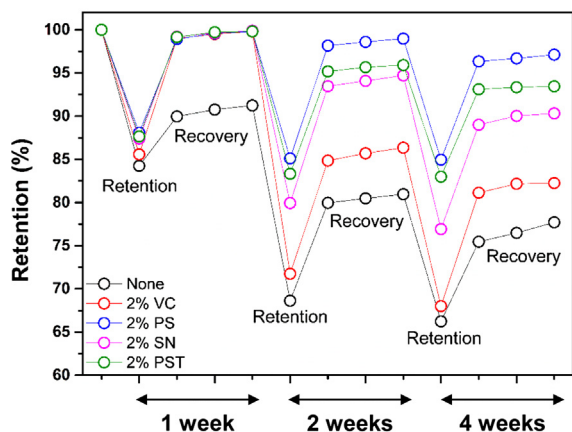
To further investigate the electrochemical behavior at elevated temperatures with different additives, graphite/NCM622 full cells with 100% SOC were exposed at 60 °C for four weeks to verify the effects of additives on the cell thickness, recovery/retention of capacity, and self-discharge behavior. The cells cycled with PS-type additives displayed less swelling than the cells cycled without PS-type additives, as shown in Fig. 8. After four weeks, the cell cycled without an additive was severely inflated, although the cells cycled with PS-type additives showed a thickness increment of 6.07%. These swelling records are in good agreement with the results, shown in Fig. 9, obtained for the retention/recovery after storage. The most effective additive was PS: cells containing PS showed excellent retention (85.0% after four weeks) and recovery



**Fig. 7.** Quantification of metal dissolution (Ni, Co and Mn) in electrolytes by ICP-MS after storage test (a) None (black), (b) VC (red), (c) PS (blue), (d) SN (pink), and (e) PST (green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



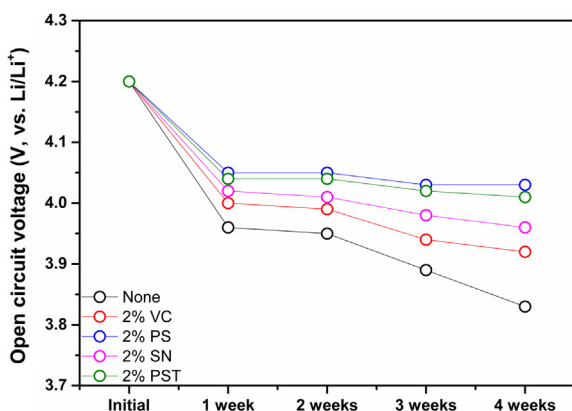
**Fig. 8.** (a) Thickness changes of pouch full cell after storage test at 60 °C.



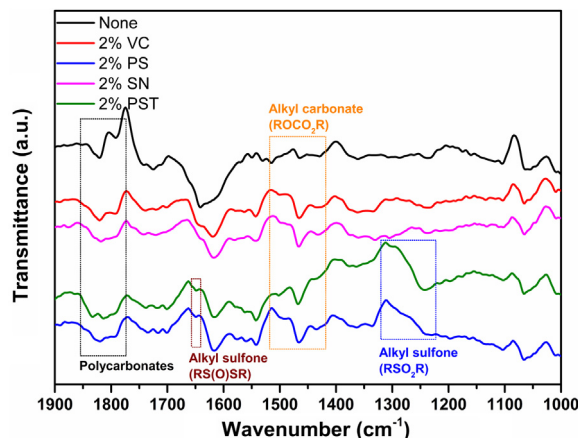
**Fig. 9.** Measurement of retention and recovery capacity after storage test at 60 °C (galvanostatic discharge–charge cycling was performed at 3.0–4.3 V), current density: 0.1 C).

(97.1% after four weeks). The cell cycled with PST also exhibited moderate retention/recovery (83.0% and 93.5%, respectively). Otherwise, the cells without PS-type additives showed considerable loss of discharge capacity, which means there was continuous undesirable reaction between the cathode and electrolyte in the cell.

The measurement of the self-discharge behavior also provided useful evidence of the function of the additives (Fig. 10). A potential drop of the cell after the turn-off current means that the electrode potential is lower because of an oxidative electrochemical reaction occurring in the cell. The cell cycled without an additive exhibited a continuous potential drop, and its electrode potential reached 3.83 V after four weeks; the cells cycled with VC and SN additives had potentials that were also less than 4.0 V, at 3.92 V and 3.96 V, respectively. In contrast, the cells cycled with the PS-type additives showed lower potential drops after one week of storage (4.05 V for PS and 4.04 V for PST), and further potential drops were negligible even four weeks later (4.03 V for PS and 4.01 V for PST). This indicates that the PS-type additives were effective in preventing undesired electrochemical reactions in the cell by forming passivation films on the cathode. According to the high-temperature storage tests, PS was the most effective additive for NCM cathodes, yielding less swelling, better retention-recovery performance, and less self-discharge as a result of enhancement in surface stability of the cathode.



**Fig. 10.** Measurement of open circuit voltage after storage test at 60 °C.



**Fig. 11.** FT-IR analysis of cathode (obtained from full-cell) after electrochemical performance at 60 °C.

To further analyze the effects of the sulfone-based additives on NCM-based cathodes, the cycled cathodes were analyzed using FT-IR spectroscopy (Fig. 11). The results of the FT-IR analysis showed the presence of polycarbonates (at 1821 cm<sup>-1</sup> and 1792 cm<sup>-1</sup>) and alkyl carbonates (at 1503 cm<sup>-1</sup>, 1466 cm<sup>-1</sup> and 1431 cm<sup>-1</sup>) that were formed by the decomposition of the primary electrolyte (EC and EMC) [29,30]. Distinctive FT-IR signals were observed for the cathodes from the PS- and PST-containing cells. Transmittance peaks were observed at 1649 cm<sup>-1</sup> and 1246 cm<sup>-1</sup>, which correspond to alkyl sulfone groups (RS(O)SR and RSO<sub>2</sub>R, respectively) [31,32]. This suggests that sulfone groups formed by electrochemical oxidation of PS and PST helped improve the performance of the NCM-based cathodes, especially at high temperatures.

#### 4. Conclusion

The use of additives to control the surface properties of NCM-based cathodes has been investigated. Of the various additives tested, the most effective are the sulfone-type additives, which yield better cycle performance (at high temperatures) and swelling properties of the NCM-based cells. The full cell cycled with PS exhibits excellent capacity retention (98.9%), a low degree of swelling after cycling (an increase in cell thickness of only 17.9%), less metal dissolution and low gas generation (56.4 kPa), even at high temperatures. Analysis of the cycled cathodes confirms that the cathode cycled with PS has a cleaner surface and higher capacity retention than the other cathodes. These results can be explained on the basis of FT-IR analysis of the cycled cathodes, which suggest that a highly desirable film consisting of alkyl sulfone components is formed on the surface of the NCM-based cathode because of the electrochemical oxidation of PS. Thus, it can be concluded that sulfone-type additives are effective in improving the performance of high-Ni-content cathodes. Further research underway in laboratory should help determine the optimal sulfone-type additive for improving the performance of such cathodes.

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